Reacties van acetyleenethers met carbonylverbindingen

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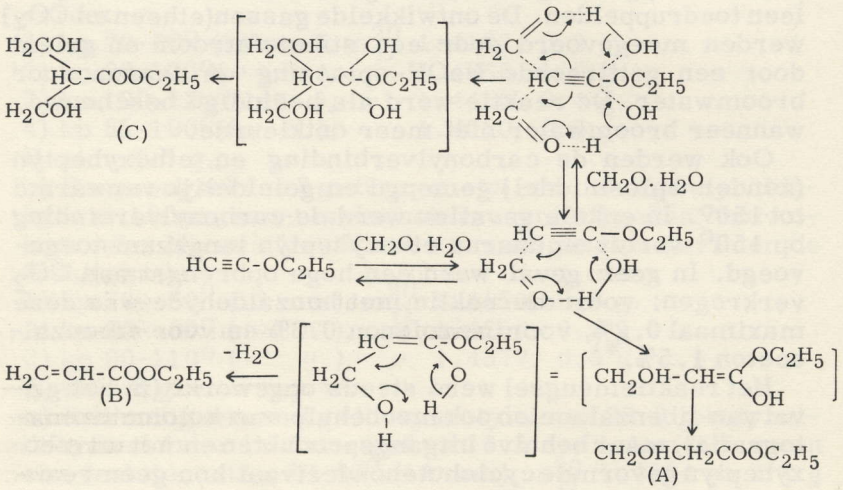
SUMMARY.

This thesis deals with a study of reactions occurring between carbonyl compounds (mainly aldehydes) and acetylenic ethers.

In chapter I we describe the reactions taking place when ethoxyethyne is shaken with an aqueous solution of formaldehyde at room temperature. The products are ethyl hydracrylate (A), ethyl acrylate (B) and ethyl α-hydroxymethyl hydracrylate (C). These substances are formed simultaneously, probably by the following reactions:



In chapter II the behaviour of ethoxyethyne towards other aldehydes and towards a few ketones, all in aqueous medium, is described. The reactions are similar to those just mentioned; the results are summarised in table I on page 17. In general lower aliphatic aldehydes react like formaldehyde, though unsaturated ones give little or no product. Aromatic aldehydes, like benzaldehyde do not react with ethoxyethyne, but from phenyl acetaldehyde a

small amount of product is obtained. The ketones investigated are unreactive, with exception of diethyl mesoxalate, which gives the expected compound. The structure of some of the products was proved by independent syntheses.

In chapter III the reactions of other acetylenic ethers R-C≡C-OR' with aqueous formaldehyde are studied. The results can be found in table III on page 33 . Obviously with increasing length of the chain R the reactivity decreases; 1-methoxy-1-heptyne was found to be unreactive.

In chapter IV other electrophylic reactions of ethoxyethyne with carbonyl compounds, viz. those in non-aqueous medium are reviewed and compared with the results mentioned in the chapters I-III.

We finally report unsuccessful attempts to perform additions of aldehydes to ethoxyethyne by free-radical reactions. Unsuccessful too were attempts to effect a reaction of ethoxyheptyne with carbonyl compounds under pyrolytic conditions.